A STATISTICAL-MECHANICS BASED LATTICE MODEL EQUATION OF STATE: APPLICATIONS TO MIXTURES WITH SUPERCRITICAL FLUIDS

Sanat K.Kumar, R.C.Reid and U.W.Suter

Department of Chemical Engineering,
Massachusetts Institute Of Technology, Cambridge, MA 02139

During the last decade, increasing emphasis has been placed on the use of the equation of state (EOS) approach to model and correlate high-pressure phase equilibrium behaviour. More successful applications have employed some form of cubic EOS (1-3) although others (e.g., 4) have been proposed. However, as the types of systems studied have become more complex, the inherent weaknesses of a cubic EOS have become apparent. We, in particular, are interested in studying phase behaviour of systems comprising polymer molecules in the presence of a supercritical fluid. Here the size disparity of the component molecules can be large. One approach would have been to adopt the modified perturbed hard chain theory (5,6) which has been adapted for mixtures of large and small hydrocarbon molecules. We, however, elected to study whether lattice theory models could be of value for systems of our interest. Studies based on this approach, have been attempted for different systems (7-11), and an interesting general model proposed by Panayiotou and Vera (12). Our approach is similar in many respects to the last reference although significant differences appear in treating mixtures.

Pure Components

Theory

Molecules are assumed to "sit" on a lattice of coordination number z and of cell size v_H. Each molecule (species 1) is assumed to occupy r_1 sites (where r_1 can be fractional), and the lattice has empty sites called holes. There are N_0 holes and N_1 molecules. To account for the connectivity of the segments of a molecule, an effective chain lenth q_1 is defined as,

$$zq_1 = zr_1 - 2r_1 + 2 \qquad 1)$$

wherein it has been assumed that chains are not cyclic. zq_1 now represents the effective number of external contacts per molecule. The interaction energy between segments of molecules is denoted by $-\varepsilon_{11}$, while the interaction energy of any species with a hole is zero. Only nearest neighbour interactions are considered, and pairwise additivity is assumed. The canonical partition function for this ensemble can be formally represented as:

$$\Omega = \sum_{\substack{\text{all} \\ \text{states } \{n\}}} \exp(-\beta E_{\{n\}}) \qquad 2)$$

where $\beta = 1/kT$. On the assumption of random mixing of holes and molecules, and following the approach of Panayiotou and Vera (12), we obtain an expression for Ω which is valid outside the critical region of the pure component, i.e.,

$$\Omega = \left(\frac{\delta}{\sigma}\right)^{N_1} \frac{(N_0 + r_1 N_1)!}{N_0!\ N_1!} \left(\frac{(N_0 + N_1 q_1)!}{(N_0 + N_1 r_1)!}\right)^{z/2} \exp\left(-\frac{\beta}{2} z N_1 q_1\, \epsilon_{11} \frac{N_1 q_1}{N_0 + N_1 q_1}\right) \qquad 3)$$

where δ is the number of internal arrangements of a molecule and σ a symmetry factor. Using the following reducing parameters

$$(z/2)\epsilon_{11} = P^* v_H = RT^* \qquad 4)$$

and defining $\underline{V}$, the total volume of the system,

$$\underline{V} = v_H(N_0 + r_1 N_1) \qquad 5)$$

an EOS that defines the pure component is obtained, i.e.,

$$\frac{\tilde{P}}{\tilde{T}} = \ln\left(\frac{\tilde{v}}{\tilde{v} - 1}\right) + \frac{z}{2} \ln\left(\frac{\tilde{v} + (q/r) - 1}{\tilde{v}}\right) - \frac{\theta^2}{\tilde{T}} \qquad 6)$$

Here θ is the effective surface fraction of molecules and the tilde ($\tilde{}$) denotes reduced variables. All quantities except v, in the EOS are reduced by the parameters in Eq.(4). The specific volume v, is reduced by v^*, the molecular hard-core volume,

$$v^* = N_1 r_1 v_H \qquad 7)$$

Expressions for the chemical potential of a pure component can also be derived from Eq.(3) and standard thermodynamics (13).

Determination of pure component parameters

In order to use the obtained EOS to model real substances one needs to obtain ϵ_{11} and v^*. For a pure component below its critical point, a technique suggested by Joffe et al., (14) was used. This involves the matching of chemical potentials of each component in the liquid and the vapour phases at the vapour pressure of the substance. Also the actual and predicted saturated liquid densities were matched. The set of equations so obtained were solved by the use of a standard Newtons method to yield the pure component parameters. Values of ϵ_{11} and v^* for ethanol and water at several temperatures are shown in Table 1. In this calculation v_H and z were set at 9.75×10^{-6} m^3 $mole^{-1}$ and 10, respectively (12). The capability of the lattice EOS to

fit pure component VLE was found to be quite insensitive to variations in z ($6<z<26$) and v_H (1.0×10^{-7} $m^3mole^{-1}<v_H<1.5\times 10^{-5}$ m^3mole^{-1}).

For SCF, the pure component parameters were obtained by fitting P-v data on an isotherm. Preliminary data for these substances suggest that although the computed v^* is a function of temperature, ε_{11} is a constant within regression error.

Discussion

In order to qualitatively understand the behaviour of the lattice EOS, it was examined in the limit of small molecules ($q,r \longrightarrow 1$). In this case Eq.(6) simplifies to the form,

$$\frac{\tilde{P}}{\tilde{T}} = \ln\left(\frac{\tilde{v}}{\tilde{v}-1}\right) - \frac{1}{\tilde{T}\,\tilde{v}^2} \qquad 8)$$

The first term can be identified with a "hard-sphere" repulsion term, while the second acconts for attractive forces. The second term can be rewritten as,

$$Z_a = \frac{P_a\, v}{R\,T} = -\frac{(P^*v^{*2})}{v^2} = -\frac{a}{v^2} \qquad 9)$$

Thus, the attractive term represented in Eq.(9) has the same form as the attractive term in the van der Waals EOS (15). On examining the data in Table 1, and computing the parameter a in Eq.(9), it was found that for variations of up to 150K, the variation of this parameter was always less than 3%, although the computed values of v^* and ε_{11} themselves showed a 7% variation. In the limit of small molecules, therefore, the lattice EOS has a term that approximates the van der Waals type attractive term closely.

The behaviour of the repulsive term of the lattice EOS is more complicated and will not be discussed in detail. At liquid-like densities this repulsion term is a better approximation to the hard spheres repulsion than the van der Waals repulsion term. At gas-like densities, however, the oppósite behaviour is observed.

Binary Mixtures

Theory

Consider a mixture of N_0 holes, N_1 molecules of species 1 and N_2 molecules of species 2. Following Panayiotou and Vera (12) the following mixing rules are assumed for the mixture parameters r_M, q_M and v_M^*.

$$r_M = \sum x_i\, r_i \qquad 10)$$

$$q_M = \sum x_i q_i \qquad 11)$$

$$v_M^* = \sum x_i v^*_i \qquad 12)$$

Lattice coordination numbers (z) and the cell volumes (v_H) for both the pure components and mixture lattices are assumed to have the same value. The partition function for this ensemble can be formulated following Eq.(2). It is assumed now that the partition function, far from the binary critical point can be approximated by its largest term. Since molecule segments and holes can distribute themselves nonrandomly, the partition function must incorporate terms to account for this effect. The nonrandomness correction Γ_{ij} allows for distribution of the segments of species i about the segments of species j over the random values of such contacts. It is defined through the equation

$$N_{ij} = N_{ij}^0 \quad \Gamma_{ij} \qquad 13)$$

where N_{ij} is the actual number of i-j contacts and N_{ij}^0 is the number of i-j contacts in the completely random case. Expressions for the nonrandomness correction must be obtained through the solution of the "quasichemical" equations(16). These equations can be solved in a closed analytic form only in the case of a two component system. In order to ensure the mathematical tractability of the binary results, it is therefore assumed that holes distribute randomly while molecules do not.

The solution for the quasichemical expressions for the pseudo two component system yields an expression for the nonrandomness correction Γ_{ij}, which can be represented mathematically as,

$$\Gamma_{ij} = \frac{2}{1 + (1 - 4\bar{\theta}_i \bar{\theta}_j (1 - g))^{1/2}} \qquad 14)$$

where,

$$g = \exp (\theta \Delta\varepsilon / kT), \qquad 15)$$

$$\Delta\varepsilon = \varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12} \qquad 16)$$

$\bar{\theta}_i$ is the surface fraction of i molecule segments on a hole-free basis and θ is the total surface area fraction of molecule segments. Eq.(16) immediately suggests a combining rule for ε_{12} as a measure of the departure of the mixture from randomness, i.e.,

$$\varepsilon_{ij} = \begin{cases} \varepsilon_{ii}, & i=j \\ 0.5 (\varepsilon_{ii} + \varepsilon_{jj}) (1 - k_{ij}), & i \neq j \end{cases} \qquad 17)$$

The mixing rule for ε arises naturally through the formulation of the canonical partition function, i.e.,

$$\varepsilon_M = \theta \sum_i \sum_j \bar{\theta}_i \bar{\theta}_j \Gamma_{ij} \varepsilon_{ij} \qquad 18)$$

An EOS for the mixture and chemical potentials for component i in the mixture can now be derived using standard thermodynamics.

$$\frac{\tilde{P}}{\tilde{T}} = \ln\left(\frac{\tilde{v}}{\tilde{v}-1}\right) + \frac{z}{2}\ln\left(\frac{\tilde{v}+(q/r)-1}{\tilde{v}}\right) - \frac{\theta^2}{\tilde{T}} +$$

$$+ 0.5zg\frac{\Delta\varepsilon}{kT}\frac{(\bar{\theta}_1\bar{\theta}_2\theta\,\Gamma_{12})^2}{(1-4\bar{\theta}_1\bar{\theta}_2(1-g))^{(1/2)}}\ln\left(\frac{\Gamma_{11}\,\Gamma_{22}}{4\,\Gamma_{12}^2\,g^{\theta}}\right) \qquad 19)$$

$$-\frac{\mu_i}{kT} = \lambda(T) + \ln q_i - \ln\theta\,\bar{\theta}_i + r_i(0.5z-1)\ln\left(\frac{\tilde{v}+(q/r)-1}{\tilde{v}}\right)$$

$$-\frac{q_i\theta^2}{\tilde{T}} + \frac{q\,\theta_i}{\tilde{T}\,\varepsilon^*}\left[2\bar{\theta}_i\varepsilon_{ii}\Gamma_{ii} + 2\bar{\theta}_j\varepsilon_{ij}\Gamma_{ij} + \bar{\theta}_1\varepsilon_{11} + \bar{\theta}_2\varepsilon_{22} - \bar{\theta}_1\varepsilon_{11}\Gamma_{11}\right.$$

$$\left. - \bar{\theta}_2\varepsilon_{22}\Gamma_{21}\right] - \left[\frac{\theta\,\Delta\varepsilon}{\tilde{T}\,\varepsilon^*} + \ln\frac{\Gamma_{11}\,\Gamma_{22}}{\Gamma_{12}^2}\right]\frac{\bar{\theta}_1\bar{\theta}_2\,\Gamma_{12}^2\,q_i}{(1-4\,\bar{\theta}_1\bar{\theta}_2(1-g))^{(1/2)}}$$

$$\left[\bar{\theta}_j\,(\bar{\theta}_j-\bar{\theta}_i)(1-g) - \bar{\theta}_1\bar{\theta}_2 g\frac{\Delta\varepsilon}{kT}\theta\,(1-\theta)\right] - \ln\Gamma_{12} - 0.5zq_i[\theta_1(1-\Gamma_{11})$$

$$\ln\frac{\bar{\theta}_1\,\Gamma_{11}}{\bar{\theta}_2\,\Gamma_{12}} + \bar{\theta}_2\,(1-\Gamma_{12})\ln\frac{\bar{\theta}_2\,\Gamma_{22}}{\bar{\theta}_1\,\Gamma_{12}}] + 0.5zq_i\left[\ln\frac{\bar{\theta}_1}{\bar{\theta}_2} - \Gamma_{11}\ln\frac{\bar{\theta}_1\Gamma_{11}}{\bar{\theta}_2\Gamma_{12}}\right]$$

$$\bar{\theta}_1\,(2\delta_{1i}-\bar{\theta}_1) + 0.5zq_i\left[\ln\frac{\bar{\theta}_2}{\bar{\theta}_1} - \Gamma_{22}\ln\frac{\bar{\theta}_2\,\Gamma_{22}}{\bar{\theta}_1\,\Gamma_{12}}\right]\bar{\theta}_2\,(2\delta_{2i}-\bar{\theta}_2) \qquad 20)$$

where μ_i represents the chemical potential of component i in a binary mixture, j=3-i and $\lambda(T)$ is some universal temperature function. δ_{ij} is the Dirac-delta function. Parameters used for obtaining these equations in a dimensionless form are defined in manner analogous to Eq.(4).

The mixture EOS [Eq. (19)] has the three terms that are present in the pure component EOS. Also, it has an additional term which accounts for the nonrandomness corrections that have been incorporated into the partition function expression. This last term, for all cases tested, is always at

least 4 orders of magnitude smaller than the other three terms and can effectively be neglected. However, it is retained for the sake of mathematical consistency.

Results and Discussion

The expressions derived for the EOS and the chemical potential of component i in a binary mixture were used to model the phase equilibria of binary mixtures. A set of non-linear equations was obtained and solved by the use of a Newton's method.

Mixtures of small molecules (acetone-benzene, ethanol-water) were considered first. In Figures 1 and 2, a comparison is made between the predicted and experimental low-pressure VLE data (17,18) for these systems. An excellent fit to the data is obtained in both cases, with the use of one apparently temperature independent parameter (k_{ij}) per binary.

The interesting aspect of this modelling is the temperature independence of k_{ij}. It was shown earlier that, if the pure components were small molecules, the lattice EOS has an attractive term with an essentially temperature independent $\underline{a}$. Extending this argument to mixtures results in the prediction of the temperature independence of k_{ij} for binary mixtures of small molecules. A temperature independent interaction parameter is a property of the binary, which could, in concept, be calculated by group contribution techniques. This scheme, if implemented, would make the modelling technique a predictive one.

In examining the sensitivity of the model to the assumed value of z, it was found for the ethanol-water system that the model predictions were insensitive to the z value in the vicinity of z=10. For large values of z (z>15), however, it was found that the model was incapable of even qualitatively prediciting mixture VLE behaviour.

The applicability of the lattice EOS in the modelling of the VLE of mixtures of molecules of different sizes was examined next. The results for the H_2S-n-heptane system at 310K and 352K are shown in Figure 3 (19). For the temperatures modelled, it is seen that there is a good agreement between the prediction and the experimental data, again with the use of one temperature independent binary interaction parameter.

The lattice model thus provides the capability to obtain good, quantitative fits to experimental VLE data for binary mixtures of molecules below their critical point. Its value lies in the fact that it performs equally well regardless of the size differences between the component molecules.

The model was then extended to the phase equilibrium modelling of solid-supercritical fluid (SCF) binaries. In Figures 4 and 5, the model behaviour is compared to experimental data for the naphthalene-carbon dioxide binary at 308 and 318K respectively. Outside the critical region, the lattice EOS provides a good fit to the measured data (20). The k_{ij} values, however,

were not temperature independent.

The agreement of the model with the data in the critical region is not satisfactory. The reason for this failure is believed to be two fold. Firstly, the partition function expression for the binary is valid in a region where the largest term in the summation in Eq.(2) dominates all other terms. In the critical region this assumption breaks down. Secondly, it has been assumed (for mathematical tractability) that holes distribute randomly while molecules do not. This assumption could be another cause of the poor fits obtained in the critical region.

In order to test the applicability of the model to polymer-SCF systems, a hypothetical system of CO_2 and a monodisperse x-mer with a monomeric unit molecular weight of 100 was simulated. Reasonable values for the pure component parameters for the polymer were chosen (12). Constant values of k_{ij} were used for the polymer system, where the degree of polymerization, x, varied between 1 and 7. It was assumed that all chains had the same ϵ, and v^* scaled as the molecular weight of the chain. Figure 6 shows the results of the predicted mole fraction of the x-mer in the SCF phase.

The model simulates an experimentally observed trend (20) that the solubility of chains in a SCF shows a strong inverse dependence on the molecular mass of the polymer. Figure 6 shows that changing the molecular weight of the chain molecule from 100 to 700 causes a reduction in solubility of nearly 6 orders of magnitude. The model also shows that all the solubility plots tend to flatten out around 300 bar, as observed in experiments. Classically used EOS like a modified cubic EOS (22), when applied to such systems, produce solubility curves which tend to show a sharp maximum around 200 bar. For polymer-SCF systems, therefore, the lattice EOS is believed to be superior to modified cubic EOS.

Conclusions

A new attempt towards the development of a statistical-mechanics based model for mixtures of molecules of disparate sizes has been made. Results obtained to date demonstrate that the lattice EOS is superior to modified cubic EOS for polymer-SCF equilibria, while for the other systems, outside the critical region, it performs as well as classically employed techniques. The removal of the assumption regarding the random mixing of holes is expected to improve the performance of the model in the critical region.

The temperature independence of the a parameter [Eq.(9)] and the binary interaction parameter (k_{ij}) for systems of small molecules are interesting phenomena that merit closer examination.

Table 1: Pure Component parameters for ethanol and water at several temperatures (z=10, v_H=9.75 x 10^{-6} m^3mole^{-1})

	Ethanol		Water	
T (K)	ϵ_{11}/k (K)	v^* (cm^3g^{-1})	ϵ_{11}/k (K)	v^* (cm^3g^{-1})
283	1357.59	1.2018	3596.56	0.9602
293	1355.47	1.2016	3516.20	0.9685
303	1314.34	1.2193	3438.16	0.9767
313	1294.18	1.2276	3362.54	0.9588
323	1274.90	1.2358	3289.36	0.9943
333	1256.49	1.2437	3218.53	1.0030
343	1238.87	1.2515	3150.14	1.0123
353	1222.04	1.2589	3083.99	1.0216
363	1205.89	1.2661	3020.02	1.0310
373	1190.43	1.2731	2958.16	1.0406
393	1161.42	1.2864	2840.43	1.0602
413	1134.68	1.2989	2730.13	1.0804
433	1109.83	1.3109	2626.57	1.1011

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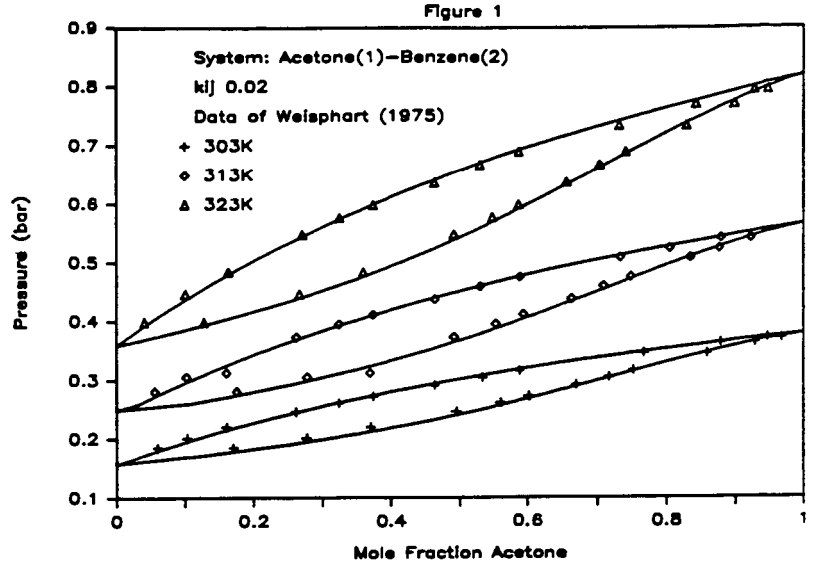

Figure 1: Comparison of lattice model prediction and experimental data of Weisphart (17) for the acetone-benzene binary at 303, 313 and 323 K (z=10, v_H=9.75 x 10^{-6} m^3mole^{-1}, k_{ij} =0.02).

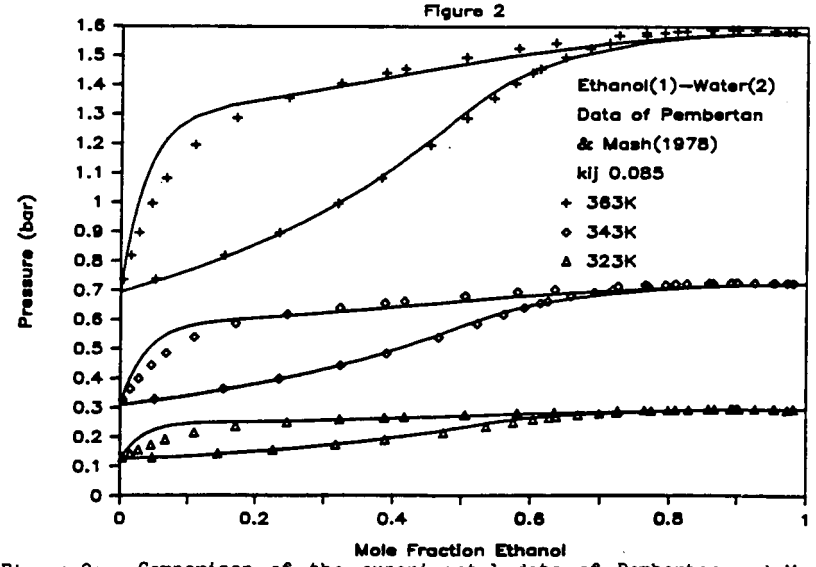

Figure 2: Comparison of the experimental data of Pemberton and Mash (18) for the ethanol-water binary at 323, 343 and 363K with the lattice model predictions with z=10, v_H=9.75 x 10^{-6} m^3mole^{-1} and k_{ij}=0.085.

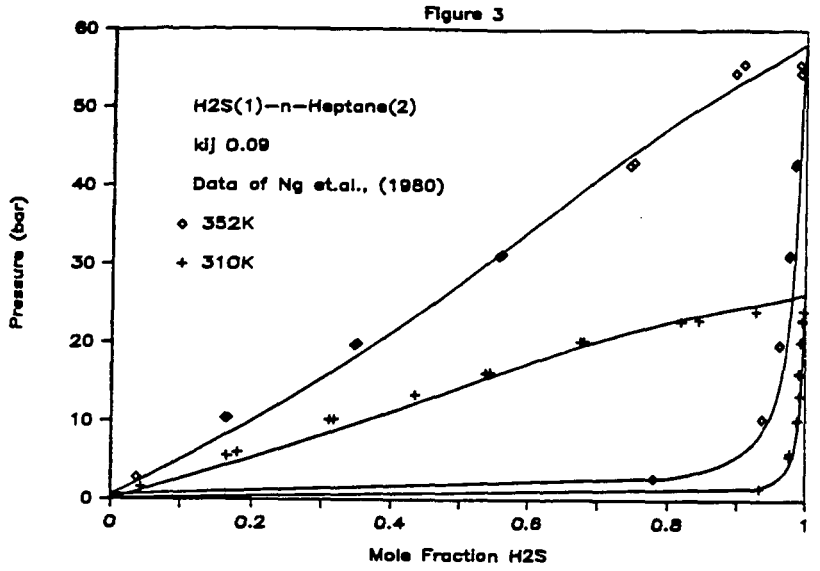

Figure 3: Comparison of the lattice model predictions and experimental data of Ng. et. al., for the H_2S- n-heptane system at 310 and 352K (z=10, v_H=9.75 x 10^{-6} m^3mole^{-1} and k_{ij}=0.09).

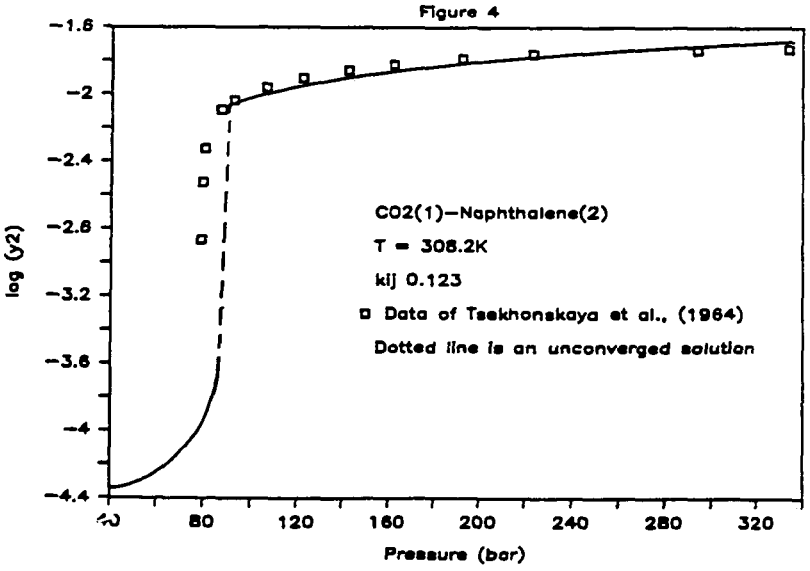

Figure 4: Comparison of the model predictions for the CO_2-napthalene binary at 308K with the experimental data of Tsekhanskaya et. al., (20).(z=10, v_H=9.75 x 10^{-6} m^3mole^{-1}, k_{ij} =0.123).

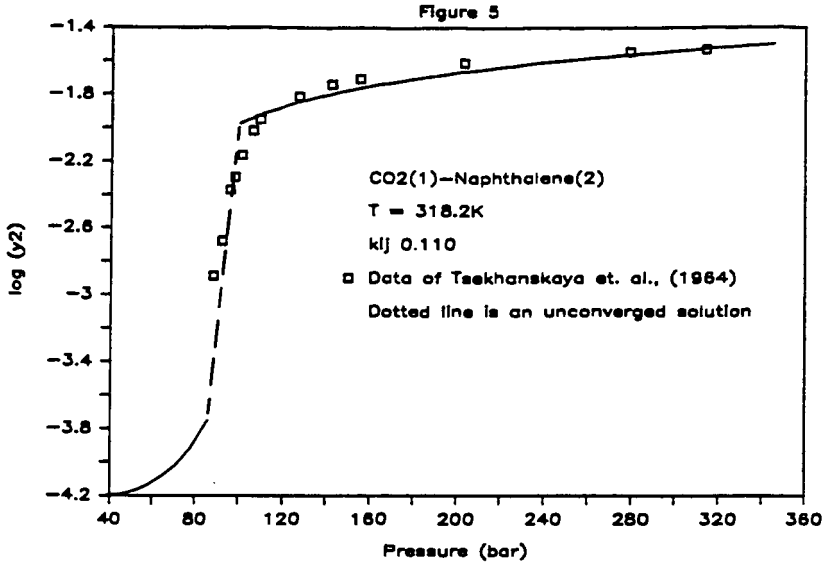

Figure 5: Comparison of the model predictions for the CO_2-napthalene binary at 318K with the experimental data of Tsekhanskaya et. al., (20). (z=10, v_H=9.75 x 10^{-6} m^3mole^{-1}, k_{ij} =0.11).

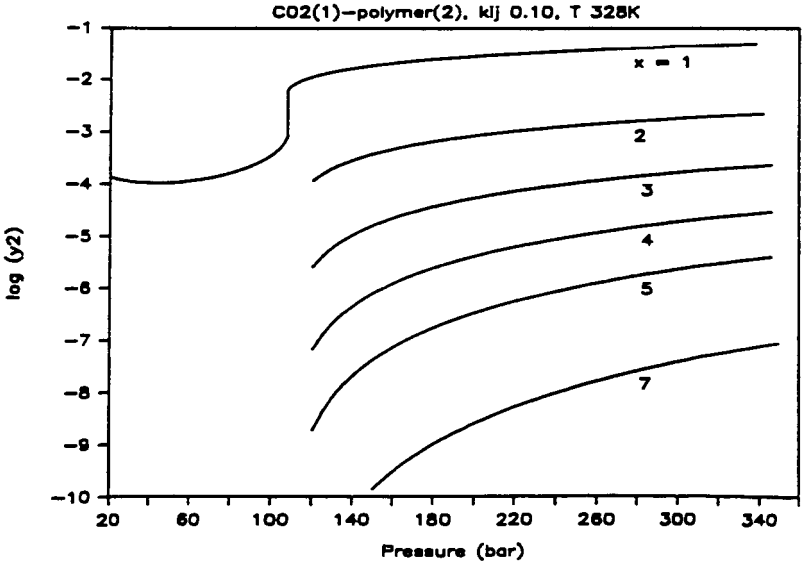

Figure 6: Lattice model predictions for the equilibrium fluid phase composition for a CO_2-polymer system at 328K. Molecular weight of a monomeric unit is 100, while the degree of polymerization, x, varies between 1 and 7. (z=10, v^H=9.75 x $10^{-6}m^3mole^{-1}$, k_{ij} =0.10).